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Storage Stability of Volatile Organic Compounds in SUMMA (Trade name) Polished Polished Canisters

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STORAGE STABILITY OF VOLATILE ORGANIC COMPOUNDS IN SUMMA® POLISHED CANISTERS

Joachim D. Pleil and Karen D. Oliver
Northrop Services, Inc. - Environmental Sciences
Research Triangle Park, North Carolina 27709

William A. McClenny
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT

Six-liter volume SUMMA polished canisters were filled with air samples containing certain volatile organic compounds (VOCs) of environmental interest at concentrations at or below 2 ppbv. Samples were periodically withdrawn from the canisters and analyzed using capillary-column gas chromatography with cryogenic sample preconcentration. The study includes analysis periods of one week and one month to determine storage stability. Synthetic VOC samples in humidified zero-grade air and spiked VOC samples in ambient air were tested. Ambient samples were prepared during peak traffic times to obtain typical air mixtures. Most compounds tested exhibited stability in concentration within typical analytical precision. This validates use of these canisters for collection of whole air samples for subsequent determination of ppbv-level VOC concentrations, at least under typical monitoring conditions.

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Introduction

One of the challenges of current ambient and indoor air monitoring is the documentation of concentrations of volatile organic compounds (VOCs). In our laboratory, VOCs from whole air samples are cryogenically preconcentrated, separated by high resolution gas chromatography, and then identified and quantified by interpretation of detector response. We report here on a series of experiments in which SUMMA® polished, stainless steel canisters are used for sample collection prior to analysis for VOCs. Ambient or simulated ambient air samples spiked with a set of 15 VOCs to concentrations of less than 2 ppbv are analyzed over time for changes in concentrations. Successful use of the canisters appears to provide a simple, convenient, and inexpensive alternative to on-site analysis. With few exceptions, artifact and contamination problems that have been reported for other sample collection procedures are not observed.

Technical Approach

Equipment

All analyses were performed using an automated Nutech 320-01 cryogenic sampling instrument (Nutech Corp., Durham, NC) equipped with a Seiscor Model VIII six port valve (Seismograph Service Corp., Tulsa, OK) and a Hewlett-Packard Model HP 588OA, Level 4 gas chromatograph with an OV-1 50-m X 0.31-mm I.D. capillary column (Hewlett Packard Corp., Avondale, PA). The column exit is split to allow simultaneous detection with a flame ionization detector (FID) and an electron capture detector (ECD). All phases of sampling from the canisters, sample preconcentration, on-column injection, and analysis were under automatic control using the programming capability of the gas chromatograph. A detailed description of this system and its automated operation is available in the literature.[1] The sample stream was dried with a Model MD-125-48(T) Perma-Pure dryer (Perma-Pure Products, Inc., Farmingdale, NJ) to avoid column or trap blockage due to ice formation. Performance and sample integrity data for these dryers are available in the literature.[2,3,4]

The sample containers were spherical 6-L stainless steel canisters (Demaray Scientific Instruments, Ltd., Pullman, WA) with stainless steel bellows valves (Nupro Co., Willoughby, OH). Internal canister surfaces were electropolished by the manufacturer using the SUMMA® process (U.S. Patent 764462) to passivate any active adsorption sites. Canisters were filled from a sample dilution manifold with a stainless steel Model MB-151 metal bellows pump (Metal Bellows Corp., Sharon, MA) through a Tylan Model FC-260 mass flow controller set at 500 mL/min. For analysis, the pressurized sample was released from the canister through a Tylan FC-260 mass flow controller set at approximately 75 mL/min and vented past the analytical system inlet. This is similar to procedures described in the literature.[5,6]

Experimental Procedures

For each experiment, canisters were cleaned and tested prior to use. Typically, four canisters were simultaneously heated to about 100°C, pumped to less than 5 Pa (40 μ Hg) pressure and sealed. This cleaning procedure usually required five to six hours. Canisters were then filled to 3 X10^5 Pa (30 psig) with zero grade nitrogen and analyzed for contamination. The cleaning procedure was then repeated and the canisters stored. Just before the canisters were used in an experiment, they were reattached to the vacuum system and pressure checked. Canisters were reprocessed (or rejected) if they exhibited contamination or a higher pressure than at the time they were sealed. Prior to filling each set of canisters, the analytical system, all related tubing, the pump, and the flow controllers were tested to ensure cleanliness.

Three separate experiments were performed to test storage stability of VOCs. In the initial experiment, seven canisters were filled with a mixture of 15 VOCs and humidified zero grade air to achieve VOC concentrations of about 2 ppbv. Canisters were filled to 30 psig using the pump and flow controller mentioned earlier. Samples from the manifold were analyzed prior to and during

the filling time to spot check input concentrations. The contents of each canister were analyzed on days 0, 2, 4, and 7 after filling.

The second experiment repeated the first; however, the VOCs were diluted with ambient air to simulate actual field conditions. Canisters were filled during peak traffic activity at the monitoring site so that typical inorganic ambient contaminants such as nitric oxide, nitrogen dioxide, carbon monoxide, etc., as well as various organic compounds would also be present in the sample. VOCs were diluted to approximately 1 ppbv each. Only four canisters were tested, again on days 0, 2, 4, and 7 after filling.

For the third experiment, three additional canisters, which had been filled along with the previous set, were analyzed on days 1, 15, and 30 after filling as a test of longer term storage stability.

Results and Discussions

VOCs used in our experiments and for which the analytical system was calibrated are listed in Table I along with typical precision values. These are expressed as a percent relative standard deviation (%RSD) of the detector response ratios, i.e., ppbv concentration divided by integrated peak area response. Numbers were based on a set of 66 span calibrations performed in pairs on consecutive working days covering a six-week period. Sample concentrations for these tests were maintained at 10.8 ppbv each for benzene, toluene, and *ortho*-xylene, at 4.2 and 3.6 ppbv each for *cis*- and *trans*-dichloropropene, respectively, and at 7.8 ppbv each for the remaining compounds. These standards were prepared in a dynamic dilution manifold from multicomponent mixtures and humidified zero air under controlled conditions. The %RSD values define the typical day-to-day system error on a set of equivalent samples. All compounds exhibit scatter less than 6.4 %RSD on the ECD and, with the exception of benzyl chloride and hexachlorobutadiene, less than 8.7 %RSD on the FID.

Table II shows the results of the initial experiment in which canisters were filled with a mixture of 15 VOCs in humidified zero grade air. The column labeled "Control Mean" shows the average of 11 analyses performed to characterize the sample, four of which were performed concurrently with filling the canisters. Since the sample was presumably of constant composition during the tests, the control means provide a way of determining any initial change in sample concentration upon filling the canisters. All canisters and runs were considered equivalent. The mean value for each compound was obtained for 28 runs, each of the seven canisters being analyzed on days 0, 2, 4, and 7. The %RSD values (as listed in Table II) show canister results to be better than or equivalent to typical system precision on both detectors, with the exception of three compounds. *cis*-1,3-Dichloropropene is only measured by the FID and shows two major outliers that contribute greatly to the %RSD. Deleting these outliers results in 5.77 %RSD instead of 43.7%. In the case of 1,2-dibromoethane, %RSD values are greater than system precision in the FID data, but not the ECD data. In both these instances we attribute the apparent lack of sample stability to interference on the FID caused by system contamination rather than canister failure. On the other hand, hexachlorobutadiene has high %RSD values on both detectors resulting from data obtained using one of the canisters that consistently yielded results seven to nine times higher than expected.

The final column in Table II shows the observed drift of compound concentrations over the seven-day storage period. These values were derived from linear regression slopes and normalized to a percent-per-day change. Typical FID and ECD drifts were less than ± 1.4% with the exception of the previously mentioned compounds and benzyl chloride. The mismatches between quoted FID and ECD concentrations for some compounds were caused by an initial calibration bias. This did not affect scatter or drift data. The problem was eliminated in the following experiments with daily calibration.

Data from the second and third experiments were treated similarly. These samples included ambient air as the dilution gas to obtain VOC concentrations of approximately 1 ppbv. The calibration compounds, benzene, toluene and o-xylene, were included in the canister analysis data though they were not spiked into the manifold. These compounds were present in the ambient air, most likely due to traffic in an adjacent parking lot. Control means consisted of averages of four analyses performed during the filling times. Since sampling occurred over only 25% of the total fill time, control means approximate the sample concentrations in the canisters only to the extent that the manifold concentrations are constant. Short-term fluctuations in the ambient air may be improperly weighted or missed entirely.

Table III shows results for the second experiment where analyses were performed on days 0, 2, 4, and 7 after filling. FID data exhibit large %RSD for vinylidene chloride, chloroform, and o-xylene. The scatter in vinylidene chloride data is most likely due to baseline interference from a poorly resolved polar compound. This has been a recurring analytical problem for certain ambient samples regardless of the sample transfer technique. The large scatter in chloroform data on the FID is not evident in the corresponding ECD data. Chloroform has a very weak FID response and is susceptible to interference from minor contaminants. Though o-xylene is generally well-behaved on the FID, in this experiment it was not a spiked compound and was present only at about 0.1 ppbv in the ambient air, close to the detection limit. ECD data showed no anomolous behavior. The mean daily drifts were within about ± 2.3% for both detectors.

Results from the third experiment are presented in Table IV. This experiment differed from the previous experiment only in the analysis times; i.e., canisters were analyzed on days 1, 15, and 30 after filling. Results indicate essentially identical behavior over this extended period with the exception of chloroform which showed less scatter on the FID, and o-xylene which showed greater scatter on the FID. Vinyl chloride and *trans*-1,3-dichloropropene were deleted from Table IV because low levels caused some peaks to miss the minimum discrimination level of the automatic integration software. Again, daily drifts over 30 days are equivalent to those observed in the previous experiment, although some large gains in o-xylene indicate further analytical problems at the very low concentrations.

Conclusions

The limited testing of SUMMA® polished canisters as documented in Tables II-IV shows that VOC concentrations of less than 2 ppbv can be adequately collected and stored for subsequent analysis. Most compounds showed storage stabilities over a seven-day period within the inherent system precision. The few anomalous results could be explained as system-related. Although one canister in the initial test showed severe contamination for one compound, subsequent cleaning and reuse in a later experiment removed this problem. Extending the storage period to 30 days yielded the same positive results; however, two compounds that were already at concentrations near the system detection limit dropped below the integration discrimination limit.

Random analytical variations and the limited data set may have strongly influenced the quoted daily drift data and may have masked true systematic changes in concentration. This is indicated by differences in magnitude and sign among the three experiments.

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Table I. Typical Instrument Precision.[a]

Compound	FID %RSD[b]	ECD %RSD
propane	7.21[c]	–
vinyl chloride	6.37	–
vinylidene chloride	7.24	–
1,1,2-trichloro-1,2,2-trifluoroethane	6.96	3.94
chloroform	6.21	3.08
1,2-dichloroethane	5.91	–
methyl chloroform	5.38	3.00
benzene	5.30	–
carbon tetrachloride	4.84	1.38
trichloroethylene	5.44	2.37
cis-1,3-dichloropropene	6.86	–
trans-1,3-dichloropropene	6.81	–
toluene	5.11	–
1,2-dibromoethane	8.08	6.21
tetrachloroethylene	6.38	3.54
chlorobenzene	8.64	–
o-xylene	6.88	–
benzyl chloride	15.83	–
hexachloro-1,3-butadiene	17.50	4.95

[a] Based on 33 pairs of daily calibrations
[b] Relative standard deviation
[c] Based on 26 pairs of daily calibrations

Table II. Canister Storage Stability Test: Spiked Humidified Zero Air Analyzed On Days 0, 2, 4 and 7 after Filling.

Compound	Control Samples Mean, ppbv (N = 11)	Canister Samples Mean, ppbv (N = 28)	Canister Samples RSD[a] %	Canister Samples Mean % change/day
FID				
propane	2.62	2.75	2.18	+0.021
vinyl chloride	1.76	1.85	4.41	+0.598
vinylidene chloride	2.03	2.13	2.09	+0.469
1,1,2-trichloro-1,2,2-trifluoroethane	1.81	1.96	2.25	+0.317
chloroform	1.88	1.97	3.44	+0.094
1,2-dichloroethane	1.79	1.87	2.54	+0.075
methyl chloroform	1.88	1.95	1.41	+0.110
benzene	–	–	–	–
carbon tetrachloride	1.98	2.04	2.85	-0.019
trichloroethylene	1.73	1.83	7.33	+0.340
cis-1,3-dichloropropene	0.77	0.86	43.7	-5.73
trans-1,3-dichloropropene	0.63[b]	0.63	8.13	-1.37
toluene	–	–	–	–
1,2-dibromoethane	1.30	1.39	14.2	-1.14
tetrachloroethylene	1.51	1.61	3.18	+0.456
chlorobenzene	1.34	1.42	6.02	+0.347
o-xylene	–	–	–	–
benzyl chloride	0.70	0.89	13.4	-3.28
hexachloro-1,3-butadiene	0.75	2.14	106.1	+5.81
ECD				
1,1,2-trichloro-1,2,2-trifluoroethane	2.18	2.31	2.32	+0.411
chloroform	2.41	2.48	1.68	+0.325
methyl chloroform	2.25	2.30	1.64	-0.154
carbon tetrachloride	1.98	2.12	2.54	+0.602
trichloroethylene	2.26	2.40	2.61	+0.696
1,2-dibromoethane	1.72	1.76	4.48	+0.067
tetrachloroethylene	1.97	2.09	2.68	+0.176
hexachloro-1,3-butadiene	0.75	1.85	97.9	+5.79

[a] Relative standard deviation
[b] N = 10

Table III. Canister Storage Stability Test: Spiked Ambient Air Analyzed on Days 0, 2, 4 and 7 after Filling.

Compound	Control Samples Mean, ppbv (N = 4)	Canister Samples Mean, ppbv (N = 16)	Canister Samples RSD[a] %	Canister Samples Mean % change/day
FID				
propane	–	–	–	–
vinyl chloride	0.76	0.76	5.26	-1.58
vinylidene chloride	1.08	2.35	36.17	+0.893
1,1,2-trichloro-1,2,2-trifluoroethane	1.04	1.17	4.27	-0.256
chloroform	1.11	2.47	37.25	+0.769
1,2-dichloroethane	0.86	0.92	3.26	-0.870
methyl chloroform	1.29	1.38	3.62	-0.652
benzene	0.31	0.36	2.78	-0.278
carbon tetrachloride	1.02	0.98	7.14	-0.102
trichloroethylene	0.96	1.01	2.97	-0.693
cis-1,3-dichloropropene	0.48	0.50	4.00	-1.20
trans-1,3-dichloropropene	0.38	0.37	8.11	-2.16
toluene	0.46	0.62	1.61	+0.322
1,2-dibromoethane	1.04	1.10	5.45	-1.45
tetrachloroethylene	0.94	0.95	3.16	-0.947
chlorobenzene	0.88	0.92	4.35	-1.41
o-xylene	0.15	0.09	22.22	-2.22
benzyl chloride	1.07	1.19	12.61	+1.68
hexachloro-1,3-butadiene	1.10	1.21	9.09	-2.15
ECD				
1,1,2-trichloro-1,2,2-trifluoroethane	1.01	1.05	1.90	+0.190
chloroform	1.04	1.00	2.00	-0.300
methyl chloroform	1.21	1.23	1.63	-0.081
carbon tetrachloride	1.23	1.23	2.44	+0.655
trichloroethylene	1.06	1.08	1.85	+0.095
1,2-dibromoethane	1.12	1.09	4.59	+0.642
tetrachloroethylene	0.93	0.94	5.32	+1.49
hexachloro-1,3-butadiene	0.96	1.00	5.00	+0.600

[a]Relative standard deviation

Table IV. Canister Storage Stability Test: Spiked Ambient Air Analyzed on Days 1, 15, and 30 after Filling.

Compound	Control Samples Mean, ppbv (N = 4)	Canister Samples Mean, ppbv (N = 9)	Canister Samples RSD[a] %	Canister Samples Mean Percent change/day
FID				
propane	–	–	–	–
vinyl chloride	0.76	–	–	–
vinylidene chloride	1.08	1.09	5.98	-0.14
1,1,2-trichloro-1,2,2-trifluoroethane	1.04	1.13	7.59	-0.44
chloroform	1.11	1.32	33.8	+1.14
1,2-dichloroethane	0.86	0.93	6.53	-0.40
methyl chloroform	1.29	1.41	6.06	-0.37
benzene	0.31	0.61	5.52	+0.18
carbon tetrachloride	1.02	0.87	10.76	-0.49
trichloroethylene	0.96	1.02	5.29	-0.38
cis-1,3-dichloropropene	0.48	0.50	7.63	+0.12
trans-1,3-dichloropropene	0.38	–	–	–
toluene	0.46	1.01	11.8	+0.67
1,2-dibromoethane	1.04	1.23	5.60	+0.10
tetrachloroethylene	0.94	1.09	3.10	-0.10
chlorobenzene	0.88	0.97	4.55	+0.24
o-xylene	0.15	0.23	65.4	+4.40
benzyl chloride	1.07	0.84	11.2	+0.36
hexachloro-1,3-butadiene	1.10	1.05	18.7	+1.17
ECD				
1,1,2-trichloro-1,2,2-trifluoroethane	1.01	0.97	2.27	-0.18
chloroform	1.04	0.97	3.56	-0.21
methyl chloroform	1.21	1.19	1.76	-0.14
carbon tetrachloride	1.23	1.59	4.12	+0.30
trichloroethylene	1.06	1.00	1.58	-0.07
1,2-dibromoethane	1.12	0.87	4.65	+0.11
tetrachloroethylene	0.93	1.01	4.88	+0.34
hexachloro-1,3-butadiene	0.96	0.98	10.14	+0.53

[a]Relative standard deviation